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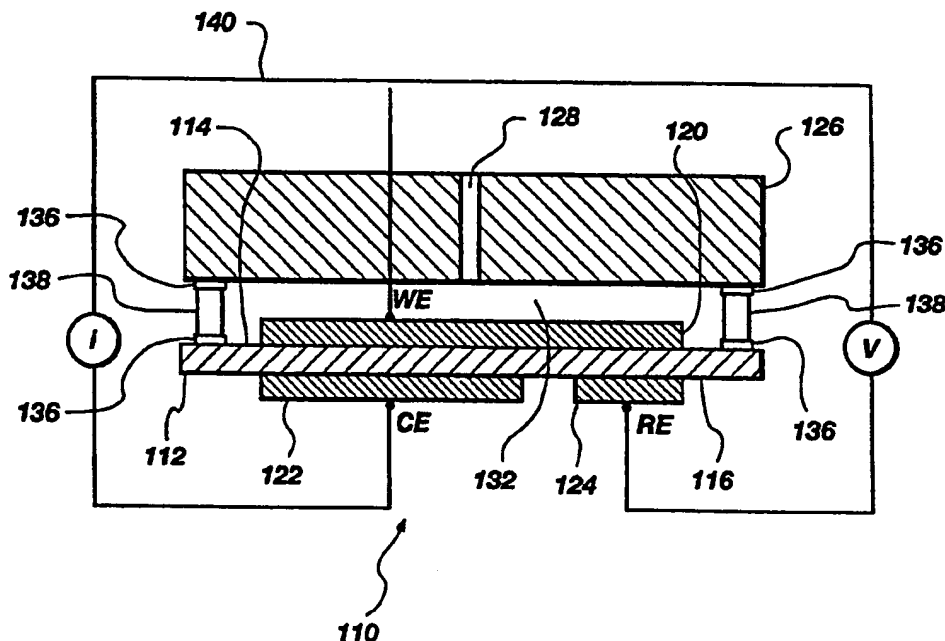
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(54) Title: MULTI-FUNCTIONAL SENSOR FOR COMBUSTION SYSTEMS

(57) Abstract

Disclosed is a multi-functional voltametric or amperometric sensor useful for sensing components of the exhaust stream of a combustion system. The disclosed sensor (110) includes a solid oxide ion-conductive electrolyte membrane (112) having two sides (114, 116). On one side is a working electrode (120), preferably covered by a diffusion barrier (126) exposed to the exhaust stream. On the other side (116), preferably exposed to air, is a counter-electrode (122) and, optionally, a reference electrode (124). Meters are provided to measure a current flux between the working and counter-electrodes.

MULTI-FUNCTIONAL SENSOR FOR COMBUSTION SYSTEMS

<u>Technical Field</u>: The invention relates generally to sensors for sensing gaseous components in the exhaust
5   stream of combustion systems, and more particularly to multi-functional sensors for combustion control systems for selective and simultaneous sensing of more than one gaseous component in the exhaust stream from a combustion system.

10   <u>Background</u>: Combustion systems convert potential chemical energy in fuels (e.g. natural gas, hydrocarbon, or hydrogen) into another form of energy such as heat or kinetic energy. The fuel is mixed with air or oxygen and combusted, whereupon the combustion products and unburned
15   fuel and air are exhausted from the system in a gaseous stream. Well-known combustion systems include a wide variety of devices including boilers, furnaces, and reciprocating engines.

       Both the efficiency and performance of a
20   combustion system can be improved by regulation of the combustion process. For example, precise control of the fuel to air ratio can significantly reduce fuel consumption, while simultaneously reducing toxic emissions in the exhaust stream. Regulation is typically
25   accomplished by a control system that monitors the concentration of combustion products such as nitrogen oxides (NO_x), carbon monoxide (CO), and unburned fuel and air in the exhaust stream. The relative concentrations of these exhaust components provides information
30   regarding the combustion system's operation. Important operating parameters such as the fuel to air ratio may then be adjusted to improve operation of the combustion system. Although the requirements of control systems are specific for each different combustion process, the
35   principles governing the control mechanism are similar.

       Several problems exist with regard to current sensing technology used in combustion control systems. Most existing sensors are capable of monitoring only a single exhaust gas component at a time in a combustion

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process. This component, typically O_2, is continuously monitored and the concentrations of other components are estimated based on mass balance and thermodynamic equilibrium. However, combustion is a highly non-

5   equilibrium process, so concentrations determined in this manner may be inaccurate. Potentiometric sensing of other combustion product gases such as NO_x, SO_x, CO_x, and H_2S, and unspent fuel gases such as CH_4 and C_3H_8, have been reported but the sensors have demonstrated limited

10   performance. Control systems could be significantly improved if several gaseous components could be accurately monitored simultaneously.

       Several *ex-situ* techniques based on optical phenomena are capable of multi-functionality, but suffer

15   from other disadvantages. For example, Fourier Transform InfraRed (FTIR), and Non-Dispersive InfraRed (NDIR) sensors can accurately monitor multiple gas concentrations, but are very large and expensive. Further, these sensors require the installation of gas

20   sampling lines which makes the sensors cumbersome, and significantly delays control system response. Other *ex-situ* techniques such as Gas Chromatography (GC), Mass Spectrometry (MS) and most traditional chemical analysis methods are less expensive but are also cumbersome and

25   time consuming. For these reasons, *ex-situ* sensors based on FTIR, NDIR, GC and MS, and traditional chemical methods are impractical for combustion control systems.

       A need exists for a simple, low-cost, multi-functional sensor capable of sensing more than one gas

30   component simultaneously. The sensor should be reliable and accurate, and be able to withstand the harsh environment of the exhaust stream from an operational combustion system.

35   DISCLOSURE OF THE INVENTION
       The invention includes a multi-functional sensor which can simultaneously sense more than one gas

component in a combustion system's exhaust stream. The
sensor is based on electrochemical principles, which
permit simplicity and low-cost in both construction and
operation. Further, the sensor uses an ion-conducting
5   solid oxide electrolyte material, which is particularly
suitable for use in the harsh temperature environment in
the exhaust stream of, for example, a natural gas
combustion system. The sensor provides increased
flexibility during operation since it is operable in
10   either a voltammetric or amperometric mode.

The sensor includes a solid oxide ion-conductive
electrolyte membrane having a first surface proximal the
exhaust gases of a combustion system, and a second
surface isolated from the exhaust gases. The first
15   surface of the membrane is associated with (e.g. adhered,
annealed, etc.) a sensing electrode including finely
divided catalyst material capable of catalyzing the
electrochemical reduction or oxidation of at least one
gaseous component from the exhaust gas stream. The
20   sensing electrode may in turn be coated with a porous
diffusion barrier to limit diffusion of certain
components in the exhaust stream to the electrode
surface. The second surface of the electrolyte membrane
is associated with a counter-electrode including finely
25   divided catalyst material suitable for catalyzing
electrochemical reduction or oxidation of the chemical
species electrochemically reduced or oxidized at the
sensing electrode. Optionally, a reference electrode may
be associated with the second surface proximal the
30   counter-electrode.

The ion-conductive electrolyte membrane is permeable
only to a specific chemical species. For example, in a
sensor for use with oxygen-containing gases (NO_x, SO_x, CO_x,
O_2, etc.), the electrolyte membrane is permeable only to
35   oxygen ions. In a sensor for use with hydrogen
containing gases (CH_4, H_2S, etc.) the electrolyte membrane
is permeable only to protons.

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It is the electrode material, however, that provides multi-function sensing operation. Different electrode materials, each highly selective for a specific gaseous component, may be integrated onto a single electrolyte membrane. In this manner, sensors highly selective for specific gaseous components may be constructed.

In operation, for example in a sensor for use with oxygen-containing gases, exhaust gases from a natural gas combustion system are allowed to contact the sensing ("working") electrode surface. A negative potential is applied to the sensing electrode to facilitate electrochemical reduction of at least one oxygen-containing gaseous component of the exhaust stream. When a negative potential sufficient to reduce an oxide to be sensed is applied to the sensing electrode (the cathode) with respect to the reference electrode (optionally contained within an enclosed air atmosphere), the oxide is reduced. The oxygen ions are then conducted through the ion-conductive electrolyte membrane to the counter-electrode (the anode) where they oxidize to oxygen molecules. Electrons involved in the reaction flow from the anode to the cathode through an electrical connection (e.g. wire) enabling measurement of an electrical current proportional to the concentration of the chemical species involved. In an exhaust stream, each oxide couple (e.g. NO_x/N_2, CO_2/CO) has a characteristic reduction potential which occurs over a potential range which depends on the concentrations of reactants and products associated with the redox reaction. It is this characteristic range that enables different redox couples to be readily distinguished from other components in the exhaust gas.

Under the condition that gas diffusion through the diffusion barrier is highly restricted, i.e., the gas mixture near the sensing electrode surface is barely convective, sensor response will show standard steady-state voltammetric waves. Current peaks will occur at discrete characteristic potentials associated with

certain oxide pairs. In a multi-component system having
multiple sensing electrodes on a single electrolyte
membrane, with each electrode highly selective for a
specific gaseous component, the diffusion of each species
5   is independent of concentration gradients of other
species. The fluxes are therefore additive making peak
currents the sum of the individual fluxes of each redox
species. In an i-E or i-t curve for a gas mixture the
peak currents for redox pairs having higher reduction
10   potentials can be corrected using the decaying current of
the previous wave as the baseline.

A given species can be distinguished by the
characteristic potential (E_p) at which current reaches a
maximum, while the species' concentration can be
15   estimated from the peak current (i_p). In general, the
peak current can be expressed by the following equation:

$$i_p = (nFA)\left(\frac{nF}{RT}\right)^{\frac{1}{2}} (vD_{gas})^{\frac{1}{2}} C_{gas} K(\alpha, \Lambda)$$

wherein n is the number of electrons involved in the
redox reaction of a particular of gas molecule, F is
Faraday's constant, A is the active surface area of
20   sensing electrode, R is the gas constant, T is the
absolute temperature, v is the potential sweep rate, D_{gas}
is the diffusion coefficient of gas molecule in the
diffusion barrier, and C_{gas} is the gas concentration in the
sample mixture. The reversibility of electrode kinetics
25   is taken into consideration by the function $K(\alpha, \Lambda)$ which
depends on the sensor's design and operating conditions
and affects the interpretation of experimental data.
However, for a given sensor and a given gas species at a
chosen potential scan rate, the peak current is directly
30   proportional to the concentration by:

$$i_p = B_1 \cdot C_{gas}$$

where constant B_1 depends upon the sensor design, the gas
species to be detected, and the potential sweep rate, can
be easily determined experimentally by calibration.

When gas diffusion through the diffusion barrier is hardly restricted, i.e., the gas mixture near the sensing electrode surface is freely convective, sensor response will show steady-state voltammetric waves under

5   convective conditions. In this case, current plateaus are expected to occur in mass-transfer-limited regions.

For a multi-component system, if the subsequent process does not commence until the current plateau has been reached of the previous process, each component gas

10   can be detected independently and distinguished by the potential at which the limiting current occurs. Each gas component's concentration can be estimated from the limiting current associated with the gas. Again, the limiting current for the subsequent process is corrected

15   by subtracting the limiting current of the previous process. In general, the limiting current (current plateaus) can be expressed as:

$$i_1 = \frac{(nFA)\, D_{gas} C_{gas}}{\delta}$$

where n, F, A, D_{gas}, and C_{gas} are as defined above and δ is the diffusion barrier's thickness. For a given sensor

20   and gas species, the limiting current is directly proportional to the concentration as determined by:

$$i_l = B_2 \cdot C_{gas}$$

where the constant B_2 is dependent upon sensor design and the gas species to be detected and can be easily

25   determined experimentally by calibration.

While the configuration of sensors for hydrogen-containing gases is similar to that for oxygen-containing gases, the electrolyte and electrode material differ. Proton conductors are employed as electrolyte membranes,

30   and the sensing electrode (the anode) consists of finely-divided particles of catalyst such as Pt, Ni, etc. (for oxidation of H_2 or hydrocarbons) deposited on the electrolyte membrane. The counter-electrode (the cathode) may also consist of Pt or Ni, and may be exposed

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to air, whereas the reference electrode is exposed to a
hydrogen-containing atmosphere. The correlation between
the sensor response (either i_t or i_p) and the
concentration of the species to be sensed is the same as
5   that described with regard to sensing of oxygen-
containing gases.

In a multi-function sensor having more than one
sensing electrode on an electrolyte membrane, the
catalysts used for a particular species absorb the
10   species at the electrode surface, while other gas
components in the mixture are barred access to the
electrode. Sensor response here relates directly to the
surface coverage θ while one obtains the gas
concentration in the exhaust mixture from a suitable
15   adsorption isotherm.

The sensor response is related to the activity a_i of
the adsorbed species which is related to the
concentration of species ι through activity coefficient Y_i
and C_i is the species concentration ι in the bulk phase.

20                               $$a_i = Y_i \cdot C_i$$

The sensor also operates in an amperometric mode
wherein a steady electrical potential is applied to the
sensor and the current response carries information about
the chemical species undergoing reduction or oxidation.
25   The advantages of amperometric sensors include fast
response, high sensitivity to the species being detected,
insensitivity to interference species, simplicity in
fabrication, high stability and reliability, and low
cost. The most attractive feature of amperometric
30   sensors is the fast response (less than 30 seconds) to
concentration changes in oxygen. Sensitivity to oxygen,
particularly in low concentration range, is also high.

BRIEF DESCRIPTION OF THE FIGURES

35   FIG. 1 is a schematic of a multi-function sensor
based on voltammetric principles for use in a control
system for natural gas combustion systems.

FIG. 2 is a schematic of a multi-function sensor installed in fluid communication with the exhaust stream from a natural gas combustion system.

FIG. 3 is schematic of a multi-function sensor with multiple electrodes based on voltammetric principles for use in a control system for natural gas combustion systems.

FIG. 4 is a steady state voltammogram of a mixture of two oxidizable species using the multi-function sensor according to the schematic in FIG. 1 under the condition that gas diffusion through the diffusion barrier is highly restricted.

FIG. 5 is a steady state voltammogram of a mixture of three oxidizable species using the multi-function sensor according to the schematic in FIG. 1 under the condition that gas diffusion through the diffusion barrier is hardly restricted.

FIG. 6 are cyclic voltammograms of a sensor in various concentrations of oxygen.

FIG. 7 plots peak current as determined from cyclic voltammograms vs. oxygen concentration in the range from 0.1% to 99% that may be used as a standard curve.

FIG. 8 are cyclic voltammograms of a sensor in air at different sweep rates from 100 to 2000 mV/s.

FIG. 9 is a plot of peak current versus the square root of potential sweep rate in mV/s ($V^{1/2}$).

FIGS. 10-14 are cyclic voltammograms of a NO sensor in gas mixtures containing different concentrations of NO.

FIG. 11A plots peak current vs. concentration of NO that may be used as a calibration curve.

FIGS. 15-18 are cyclic voltammograms of a NO sensor in gas mixtures containing various concentrations of oxygen and NO.

FIGS. 19-22 are cyclic voltammograms of a NO sensor in gas mixtures containing various concentrations of oxygen and NO.

FIGS. 23-26 are cyclic voltammograms of a NO_x sensor
in an NO concentration of 1000 ppm and a sweep rate of
100 mV/s at different temperatures from 350 to 500°C.

FIGS. 27-32 are cyclic voltammograms of a NO_x sensor
at 500 ppm NO with various added concentrations of
interfering species CO_2, CH_4, CO and H_2.

FIGS. 33-36 are cyclic voltammograms of a NO_x sensor
at varying added concentrations of H_2O vapor.

FIGS. 37-40 are cyclic voltammograms of a NO_x sensor
at NO concentrations from 100 ppm to 500 ppm in a
constant mixture of interfering species CO_2, CH_4, O_2, and
H_2O.

FIGS. 41-44 are cyclic voltammograms of a NO_x sensor
at constant NO, CO_2, CH_4, and H_2O concentrations and
varying concentrations of O_2 from .2% to 4.2%.

FIGS. 45-48 are cyclic voltammograms of a NO_x sensor
at 1000 ppm NO and 800 ppm NO + 0.4% O_2 after storage in
ambient atmosphere for 3 months.

BEST MODE OF THE INVENTION

Referring to FIGS. 1 and 2, a multi-functional
sensor 110 for a natural gas combustion system includes
an ion-conductive electrolyte membrane 112 constructed
from ceramic solid oxide material. The particular
composition of the electrolyte membrane may vary
according to the requirements of particular applications,
and specific materials will be discussed later with
regard to specific embodiments. Electrolyte membrane 112
has a first surface 114 proximal the exhaust stream from
a natural gas combustion system, and an opposing second
surface 116 isolated from the exhaust stream. A sensing
electrode 120 adheres to at least a portion of first
surface 114 of the electrolyte membrane, and a counter-
electrode 122 adheres to a portion of the second surface
116. The sensing electrode includes a porous layer of
catalytic material (e.g. a vanadia based material) atop a
substrate made of fine particles of conductive material
(e.g. palladium or platinum). The specific composition

of both sensing and counter-electrodes 120 and 122 also
may vary according to the requirements of particular
applications, and will also be discussed later with
regard to specific embodiments. A reference electrode
5   124 (made of e.g. platinum) may be adhered to the second
surface 116 proximal the counter-electrode.

Sensing electrode 120 may be covered by a porous
diffusion barrier 126 which limits the amount of exhaust
gas that may diffuse to the sensing electrode. In a
10   preferred embodiment, the diffusion barrier is
constructed from the same material as the electrolyte
membrane to eliminate complications from thermal
expansion mismatches and to avoid chemical interactions.
Alternatively, the diffusion barrier may be constructed
15   from alumina. A laser bored diffusion aperture 128,
typically less than 30 microns (μ) in diameter,
establishes fluid communication between the exhaust
stream and the sensing electrode 120. Methods other than
laser boring, such as fiber-introduction during casting,
20   may also be used to create the diffusion aperture.

In a preferred embodiment best illustrated by FIG.
1, an exhaust gas compartment 132 in fluid communication
with the exhaust stream is disposed between diffusion
barrier 126 and electrolyte membrane 112. Fluid access
25   to the exhaust gas compartment may be had through
diffusion aperture 128. The exhaust gas compartment
allows exhaust gases entering through diffusion aperture
128 to diffuse out and contact a larger area of the
sensing electrode 120. Exhaust gas compartment 132 is
30   sealed around its edges to the diffusion barrier 126 and
the electrolyte membrane 112 by glass seals 136 at the
ends of ceramic spacers 138. Thus, the atmosphere inside
the exhaust gas compartment is limited to exhaust gases
that diffuse in through the diffusion aperture.
35   Sensing electrode 120, counter-electrode 122, and
reference electrode 124 are electrically connected via
electrical connection means 140 enabling a voltage

potential indicated by reference letter **V** to be applied
between the sensing electrode and the reference
electrode. If no reference electrode is present, this
potential is applied between the sensing and counter
5   electrodes. The electrical connection means also
enables an electrical current indicated by reference
letter **i** to flow between the sensing electrode and the
counter-electrode. Preferably, electrical connections
are silver wire of 0.25 mm (0.01") in diameter, connected
10 to the electrodes with a small amount of silver paste.
The resulting connections may be fired at 500°C for 30
minutes to set-up the silver paste, and bond the
electrical connections to the electrodes.

In a preferred installation configuration best
15 illustrated in FIG. 2, the sensor **110** is mounted in the
wall **144** of the exhaust pipe from a natural gas
combustion system. Exhaust gases from the exhaust stream
are in fluid communication with the diffusion barrier
126, and thus free to diffuse through diffusion aperture
20 **128** to sensing electrode **120**, while both counter-
electrode **122** and reference electrode **124** are isolated
from the exhaust stream in a separate air atmosphere.
Such a configuration is optional though, and the counter
and reference electrodes may also be in fluid
25 communication with the exhaust stream.

Referring now to FIG. 3, a multi-electrode
embodiment having a plurality of different sensing
electrodes SE_1-SE_4 is schematically illustrated. Each
sensing electrode may be constructed from a material
30 having a high selectivity for a specific component in the
exhaust gas stream. High selectivity to a chemical
species results from specific adsorption of the chemical
species at a catalyst. For example, the catalysts used
for NO_x sensors strongly adsorb NO_x at the electrode
35 surface, whereas other gas components in the mixture are
physically inaccessible to the electrode. In this
manner, sensors highly selective to, e.g. NO_x, CO,

unburned hydrocarbons, and other combustion products can
be constructed.

In operation, exhaust gases from the combustion
system diffuse through diffusion aperture 128 into the

5   exhaust gas compartment 132 where they contact the
sensing electrode 120. In a sensor for oxygen-containing
gases (NO_x, CO_2, O_2, CO, etc.), a negative voltage
potential is applied to sensing electrode 120 with
respect to reference electrode 124 which is exposed to

10   air. In a sensor for hydrogen containing gases (CH_4, H_2S,
and other hydrocarbons), a positive voltage potential is
applied to sensing electrode 120 with respect to
reference electrode 124 which is exposed to a hydrogen-
containing atmosphere. The counter-electrode 122 in both

15   cases may be exposed to air.

In the case of a sensor for oxygen-containing gases
operating in voltammetric mode, when a negative potential
sufficient to reduce an oxide to be sensed is applied to
sensing electrode 120 (the cathode), the oxide is

20   reduced, and the oxygen ions move through ion-conductive
electrolyte membrane 112 to counter-electrode 122 (the
anode) where they are oxidized to oxygen molecules in the
air environment. In the case of a sensor for hydrogen-
containing gases operating in voltammetric mode, when a

25   positive potential sufficient to oxidize a hydrogen-
containing chemical species to be sensed is applied to
sensing electrode 120 (the anode), the species is
oxidized, and the protons move through the electrolyte
membrane to counter-electrode 122 (the cathode) where

30   they are reduced to hydrogen molecules. Electrons
involved in the redox reactions move from anode to
cathode through electrical connection means 140 enabling
measurement of an electrical current, the magnitude of
which is proportional to concentration of the chemical

35   species involved in the redox reaction.

In the voltammetric mode, sensor response is
dependent upon the exhaust stream's flow pattern. The

flow pattern can be regulated, however, by the
configuration of diffusion barrier **126** and the pore size
of diffusion aperture **128**. Under the condition that
exhaust gas diffusion through diffusion barrier **126** is
highly restricted (i.e. a small diffusion aperture), the
gas mixture near the surface of sensing electrode **120**
will be barely convective. In this case, sensor response
will show standard steady-state voltammetric waves with
current peaks at discrete characteristic potentials
associated with certain chemical species. For a multi-
component system, if the diffusion of each species is
independent of concentration gradients of other species,
the fluxes are additive and the i-E or i-t curves for the
mixture are the sum of the individual i-E curves of each
species as illustrated in FIG. 4. The peak currents for
the subsequent species must be corrected using the
decaying current of the previous wave as the baseline.
Accordingly, a given chemical species can be
distinguished by the characteristic potentials (E_p) at
which current reaches a maximum while the species'
concentration can be estimated from the peak current (I_p).

Under the condition that exhaust gas diffusion
through diffusion barrier **126** is hardly restricted (i.e.
a large diffusion aperture), the gas mixture near the
surface of sensing electrode **120** will be freely
convective. In this case, sensor response will show
steady-state voltammetric waves under convective
conditions, with current plateaus expected to occur in
mass-transfer-limited regions. For a multi-component
system, if the subsequent process does not commence until
the current plateau has been reached for the previous
process, each component gas can be detected independently
and distinguished by the potential at which the limiting
current occurs as illustrated in FIG. 5. The
concentration of each gas component can be estimated from
the limiting current associated with the gas. Again, the
limiting current for the subsequent process has to be

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corrected by subtracting the limiting current of the
previous process.

        In the case of a multi-function sensor having a
plurality of different sensing electrodes such as
5   illustrated in FIG. 3, each electrode has high
selectivity for a specific gas component in the exhaust
stream. Due to the fact that electrode kinetics can
significantly shift the potential from the thermodynamic
value at which redox reactions occur, this potential
10   shift can be tailored by means of electrocatalysis to
detect each gas component in the exhaust stream
selectively. The high selectivity to a chemical species
stems from the specific adsorption of the species at the
catalyst. The sensor response is thus directly related
15   to the surface coverage, while the gas concentration is
obtainable from a suitable adsorption isotherm such as
the Langmuir isotherm.

        The composition of both ion-conductive electrolyte
and electrode materials may be varied according to the
20   requirements of particular applications. In principle,
any suitable oxygen anion conductors can be used for
oxygen containing gases, and, any suitable proton
conductors can be used as electrolyte for hydrogen-
containing gases. For example, zirconia-based ceramics
25   such as tape-cast yttrium-strontium-zirconium (YSZ) with
a thickness less than 0.2 mm, and thoria-based ceramics
are suitable electrolyte materials for voltammetric
sensors for oxygen containing gases. Isopressed pellets
of $BaCeO_3$, and $SrCeO_3$ (yttria or Nd-doped) are suitable
30   electrolyte materials for sensors for hydrogen and
hydrocarbons. Electrode materials suitable for oxygen-
containing gases include noble metals (Pt, Ag, Au, etc.),
perovskites (LSM, LSCo, and modified LSM and LSCo, etc.),
and other mixed oxides and transition metal sulfides and
35   of mixture of them. Electrode materials suitable for
reduction of NO_x, SO_x, CO_2, H_2O, as well as for oxidation
of H_2, CH_4 and other unburned hydrocarbons include

alumina-iron bases catalysts, vanadia based catalysts
(V_2O_5/TiO_2, V_2O_5/Al_2O_3, V_2O_5/SiO_2, etc.), nickel-based
catalysts, and rare earth metals or other metal oxide
based catalysts and the mixture of them. V_2O_5 based
5   catalysts containing 50% of solid, which consists of 10
mol% of V_2O_5 and 90 mol% TiO_2 is a suitable catalyst for
sensors detecting NO_x and O_2.

The sensor can be operated in an amperometric mode
whereby a steady electrical potential is applied to the
10   sensor and the current response carries information about
the chemical species undergoing reduction or oxidation.
Amperometric sensors based on bismuth oxide-based ionic
conductors have the attractive features of fast response
(less than 30 seconds) and high sensitivity to oxygen,
15   particularly in low concentrations.

The invention is further explained by the following
illustrative examples.

EXAMPLE I

Several batches of voltammetric sensors were
20   fabricated, arranged as per FIG. 1, having diffusion
barriers made in different ways (laser-drilled and fiber-
introduced holes) and having varying pore sizes (e.g.
from 10 to 200 μ m). Several typical voltammograms from
these sensors are illustrated in FIG. 6 (O_2-N_2 mixture at
25   450°C with a sweep rate of 100mV/s).

Fabricated sensors were positioned in a quartz tube
which was placed in a tubular furnace controlled at a
constant temperature. Pre-mixed sample gases were flowed
through the quartz tube at a controlled flow rate,
30   typically from 60 to 150 cc/min. Each and every gaseous
component in the mixture is adjustable individually.

A potentiostat/galvanostat (EG&G PAR 273) interfaced
with a computer (IBM 286) was used to sweep the potential
and to collect the current response of sensors under
35   testing. The voltammograms were displayed on the
computer screen after each potential sweep, and were
recorded by a printer (FIG. 6).

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A typical plot of peak current, as determined from cyclic voltammograms, versus oxygen concentration in the range from 0.1% to 99% is depicted in FIG. 7. Clearly, the peak currents, i_p, depend linearly on $-\ln(1-X_{O2})$ over

5   a wide concentration range, where X_{O2} is the molar fraction of oxygen in the gas mixtures. This also indicates that the oxygen transports through the diffusion aperture by normal diffusion.

     FIG. 8 are some cyclic voltammograms of a sensor

10   according to the invention in air at different sweep rates, from 100 to 2000 mV/s. The sharp current peaks for oxygen reduction at potential sweep rate of 2000 mV/s indicate that, in principle, this sensor is capable of generating a sensing signal in less that one second. In

15   addition, as shown in FIG. 9, the peak current (mA) versus $V^{\frac{1}{2}}$ (square root of potential sweep rate in mV/s) of a voltammetric sensor according to the invention in air at 500°C has a linear relationship, indicating that the reduction waves are in good shape.

20   FIGS. 10-14 are typical voltammograms of a V_2O_5 coated NO sensor in gas mixtures containing different concentrations of NO at 500°C and 100 mV/s. Clearly, the sensor responded to NO very well at about -0.8 V and peak current changed according to the concentration of NO.

25   The linear relationship between peak current and concentration NO shown in FIG. 11A can be used as a calibration curve.

EXAMPLE II
Selectivity of Sensor

30   FIGS. 15-22 are voltammograms of a NO sensor in gas mixtures containing various concentrations of oxygen and NO. First of all, the sensor's selectivity to NO in a gas containing both NO and O_2 is about 10 times better than the selectivity to O_2. As shown in FIGS. 19-20, the

35   response of the sensor to oxygen concentrations less than 2000 ppm is barely observable. Thus, when the concentration of O_2 is less than 2000 ppm, oxygen has no

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effect on detection of NO. Secondly, the reduction
potential for oxygen is well separated from the reduction
potential for NO so that NO can be detected in the
presence of oxygen. For example, as shown in FIG. 15,
5   the sensor's response to 50 ppm of NO is still observable
even in the presence of 1.9% oxygen. Additionally,
FIG. 6 shows that CO, CO_2, and hydrocarbons have no
interference to the measurement of O_2 and NO.

EXAMPLE III

10   ### Temperature Dependence

Temperature dependence of peak current over the
temperature range from 350 to 500°C is shown in FIGS.
23-26. Clearly, as the operating temperature increases,
the signal to noise ratio also increases.

15   ## EXAMPLE IV

Effect of Interfering Species

The effect of interfering species such as CO_2, CH_4,
CO, H_2 and H_2O to NO_x sensors was studied individually.
Voltammograms were taken after one hour of introduction
20   of interfering species to gas mixtures. As shown in
FIGS. 27-30, sensor performance was barely affected by
adding 10% CO_2, 500 ppm CH_4 and 500 ppm CO gases into 500
ppm NO_x gas. The existence of 500 ppm hydrogen, however,
showed significant effect on the sensor's response to NO_x
25   as shown in FIG. 31. One plausible explanation could be
that the hydrogen introduced reacted directly with the NO_x
in the sample gas. Fortunately, the effect of hydrogen
on sensor response to NO_x was eliminated by introducing a
small amount (0.7%) of oxygen into the gas mixture, as
30   shown in FIG. 32. Since a small amount of oxygen is
present in an actual combustion system exhaust, the
effect of hydrogen on sensor performance can be managed.

Water vapor was introduced into gas mixtures by
bubbling nitrogen gas through a water bath kept at
35   constant temperature. The main impact of water vapor was
to increase the background current of voltammograms as

shown in FIGS. 33-36. The NO_x signal, however, can still
be determined among the background.

EXAMPLE V

Other Gases

5   The simultaneous effect of other gases on an NO_x
sensor was further studied by testing sensor performance
in gas mixtures containing CO_2, CH_4, O_2, and H_2O. Two
special cases were investigated in detail. Sensor
response to changes in NO_x concentration was studied when
10   the concentrations of all other gases were kept constant.
The sensor response is shown in FIGS. 37-40. Clearly,
with the existence of 10% CO_2, 100 ppm CH_4, 0.4% O_2 and 3%
H_2O, the sensor still responded to NO_x very well from 500
ppm to 100 ppm. Sensor response to changes in oxygen
15   concentration was studied when the concentrations of all
other species were kept constant. The sensor response in
shown in FIGS. 41-44. When the concentration of NO_x was
kept at 330 ppm in the gas mixtures, the oxygen signal
can be easily determined when its concentration was
20   higher than 0.2%. The current peak for NO_x was still
obvious even with the existence of 4.2% oxygen. The
position of the NO_x current peak also did not move when
the oxygen concentration was changed from 0.2% to 4.2% in
the gas mixtures. In both cases, no other peaks appeared
25   in the voltage range studied other than the peaks due to
the reduction of NO_x and O_2, indicating that the sensor
was inert to the other gases such as CO_2 and CH_4.

       Although the invention has been described with a
certain degree of particularity, this has been to
30   illustrate the invention's principles, and should not be
construed as limiting. Various changes and modifications
can be made without departing from the scope of the
appended claims.

-19-

CLAIMS

What is claimed is:

1. A multi-functional sensor for sensing gaseous
components in an exhaust stream from a combustion system
comprising:

a solid electrolyte membrane comprised of an ion-
            conductive oxide material and having a
            thickness for selectively conducting a gaseous
            component through said thickness, and further
            having a first surface proximal said exhaust
            stream, and a second surface opposite said
            first surface and isolated from said exhaust
            stream;

a sensing electrode associated with the first surface of
            said solid electrolyte membrane and in fluid
            communication with said exhaust stream, said
            sensing electrode comprised of a substrate of
            finely divided conductive particles underneath
            a catalyst capable of catalyzing a first
            oxidation or reduction reaction, respectively,
            of a specific gaseous component in the exhaust
            stream;

a counter-electrode associated with said second surface
            of said solid electrolyte membrane, said
            counter-electrode comprised of finely divided
            particles of an electrode material capable of
            catalyzing a reduction or oxidation reaction,
            respectively, of the specific gaseous
            component, opposite to that of that of the
            oxidation or reduction reaction occurring at
            the sensing electrode;

means for electrically connecting said sensing electrode
            and either the counter-electrode or other
            electrode on the second surface of said
            electrode membrane for enabling application of
            an electrical potential across said sensing

-20-

electrode and other electrode, and for enabling
a current flux to flow between the sensing and
counter-electrodes; and

a meter for determining current flux between said sensing
electrode and said counter-electrode.

2.   The multi-functional sensor of claim 1 further
including a reference electrode associated with the
second surface and in fluid communication with a gas
suitable for reference, and serving as the other
electrode for the electrical connection, said reference
electrode comprised of a noble metal.

3.   The multi-functional sensor of claim 1 further
comprising a diffusion barrier covering said sensing
electrode for limiting the amount of exhaust gas in fluid
communication with said sensing electrode, said diffusion
barrier having a aperture therein in fluid communication
with the exhaust stream.

4.   The multi-functional sensor of claim 3 further
comprising an exhaust gas compartment disposed between
said diffusion barrier and said electrolyte membrane and
in fluid communication with said aperture.

5.   The multi-functional sensor of claim 2 wherein
said reference electrode is in fluid communication with
air isolated from the exhaust stream.

6.   The multi-functional sensor of claim 2 wherein
said reference electrode is in fluid communication with
an exhaust stream containing hydrogen gas.

7.   The multi-functional sensor of claim 1 wherein
said sensing electrode is highly selective for the
oxidation or reduction of a specific component of said
exhaust stream.

8.   The multi-functional sensor of claim 7 including
a plurality of said sensing electrodes, each said sensing
electrode having high selectivity for electrochemical
reduction or oxidation of a particular component of said
5   exhaust stream.

9.   A multi-functional sensor for sensing oxygen-
containing gaseous components in an exhaust stream from a
combustion system comprising:
10   a solid electrolyte membrane having a thickness and
               comprised of an ion-conductive oxide material
               selectively conducting oxygen ions through said
               thickness, and further having a first surface
               proximal said exhaust stream, and a second
15   surface opposite said first surface and
               isolated from said exhaust stream;
     a sensing electrode associated with said first surface of
               said solid electrolyte membrane and in fluid
               communication with said exhaust stream, said
20   sensing electrode comprised of a substrate of
               finely divided conductive particles underneath
               a catalyst capable of catalyzing
               electrochemical reduction of an oxygen-
               containing gaseous component in the exhaust
25   stream;
     a counter-electrode associated with the second surface of
               said electrolyte membrane, said counter-
               electrode comprised of finely divided particles
               of an electrode material suitable for
30   catalyzing electrochemical oxidation of oxygen
               ions conducted through said thickness of said
               solid electrolyte membrane;
     electrical connection means for electrically connecting
               said sensing electrode and either the counter-
35   electrode or another electrode on the second
               surface of said electrode membrane for enabling
               application of an electrical potential across

said sensing electrode and other electrode, and
for enabling a current flux to flow between the
sensing and counter-electrodes;
a meter for determining current flux between the sensing
electrode and said counter-electrode;
a diffusion barrier covering said sensing electrode for
limiting the amount of exhaust gas in fluid
communication with said sensing electrode, said
diffusion barrier having an aperture therein in
fluid communication with the exhaust stream;
and
an exhaust gas compartment disposed between said
diffusion barrier and said electrolyte membrane
and in fluid communication with said diffusion
aperture for receiving a portion of said
exhaust gases in said exhaust stream through
said diffusion aperture.

10. The multi-functional sensor of claim 9 wherein
said sensing electrode selectively electrochemically
reduces a specific oxygen-containing component of said
exhaust stream.

11. The multi-functional sensor of claim 9
including a plurality of said sensing electrodes, each
said sensing electrode being high selectivity for
electrochemical reduction of a specific oxygen-containing
component of said exhaust stream.

12. A multi-functional sensor for sensing hydrogen-
containing gaseous components in an exhaust stream from a
combustion control system comprising:
a solid electrolyte membrane having a thickness and
comprised of an ion conductive oxide for
selectively conducting protons through said
thickness, and having a first surface proximal
said exhaust stream, and a second surface

opposite said first surface and isolated from
said exhaust stream;

a sensing electrode associated with said first surface of
said solid electrolyte membrane and in fluid
5   communication with said exhaust stream, said
sensing electrode comprised of a substrate of
finely divided conductive particles underneath
a layer of catalyst capable of catalyzing
electrochemical oxidation of a hydrogen-
10   containing gaseous component;

a counter-electrode associated with the second surface of
said solid electrolyte membrane, said counter-
electrode comprised of finely divided particles
of an electrode material capable of catalyzing
15   electrochemically reducing the protons
conducted through the thickness of said solid
electrolyte membrane;

electrical connection means for electrically connecting
said sensing electrode and either the counter-
20   electrode or another electrode on the second
surface of said electrode membrane for enabling
application of an electrical potential across
said sensing electrode and other electrode, and
for enabling a current flux to flow between the
25   sensing and counter-electrodes;

a meter for determining the current flux between said
sensing electrode and said counter-electrode;

a diffusion barrier covering said sensing electrode for
limiting the amount of said exhaust gas in
30   fluid communication with said sensing
electrode, said diffusion barrier having an
aperture extending therethrough in fluid
communication with the exhaust stream; and

an exhaust gas compartment disposed between said
35   diffusion barrier and said electrolyte membrane
and in fluid communication with said aperture

for sampling a portion of the exhaust gases in
the exhaust stream through the aperture.

13. The multi-functional sensor of claim 9 or claim
12 further including a reference electrode associated
with the second surface and in fluid communication with a
gas suitable for reference, and serving as the other
electrode for the electrical connection, said reference
electrode comprised of a noble metal.

14. The multi-functional sensor of claim 2 or claim
13 wherein said reference electrode is platinum.

15. The multi-functional sensor of claim 12 wherein
said sensing electrode has high selectivity for
electrochemically oxidizing a specific hydrogen-
containing component of said exhaust stream.

16. The multi-functional sensor of claim 15
including a plurality of said sensing electrodes, each
said sensing electrode having high selectivity for
electrochemically oxidizing a specific hydrogen-
containing component of said exhaust stream.

17. The multi-functional sensor of claim 3, claim
12 or claim 17 wherein said diffusion barrier comprises
an alumina.

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Fig. 1

144

COMBUSTION
EXHAUST
STREAM

126   114   120   112

116   122   124

V applied

i measured

110

Fig. 2

COMBUSTION
EXHAUST
STREAM

im, 1   Va, 1
im, 2   Va, 2
im, 3   Va, 3
im, 4   Va, 4

SE_1 SE_2 SE_3 SE_4

CE   RE
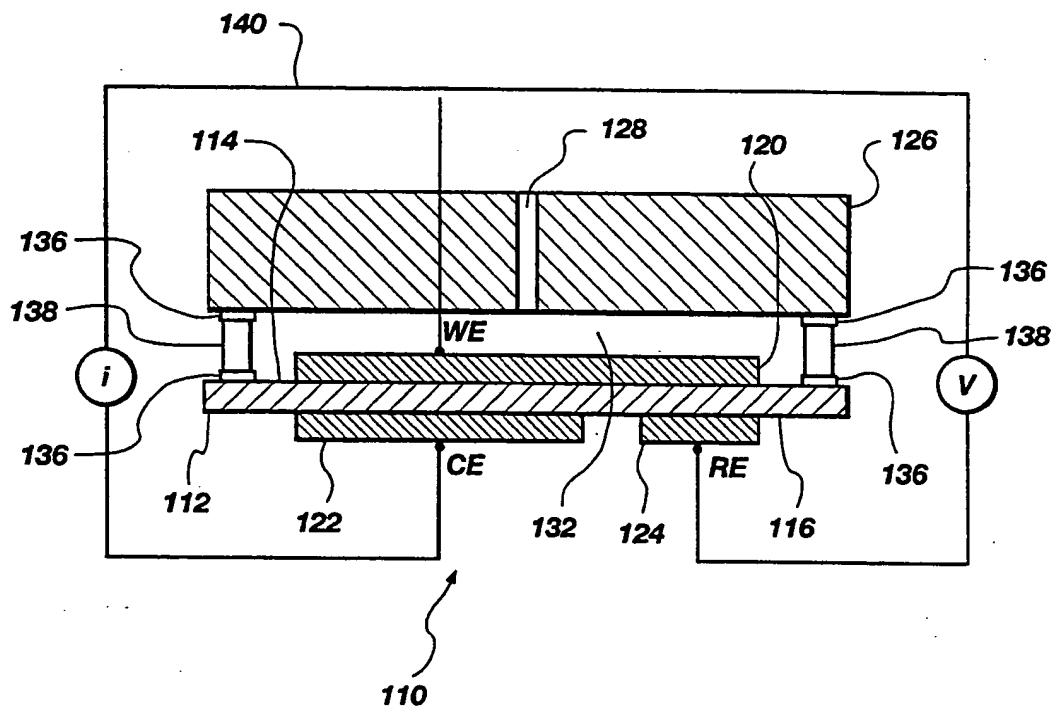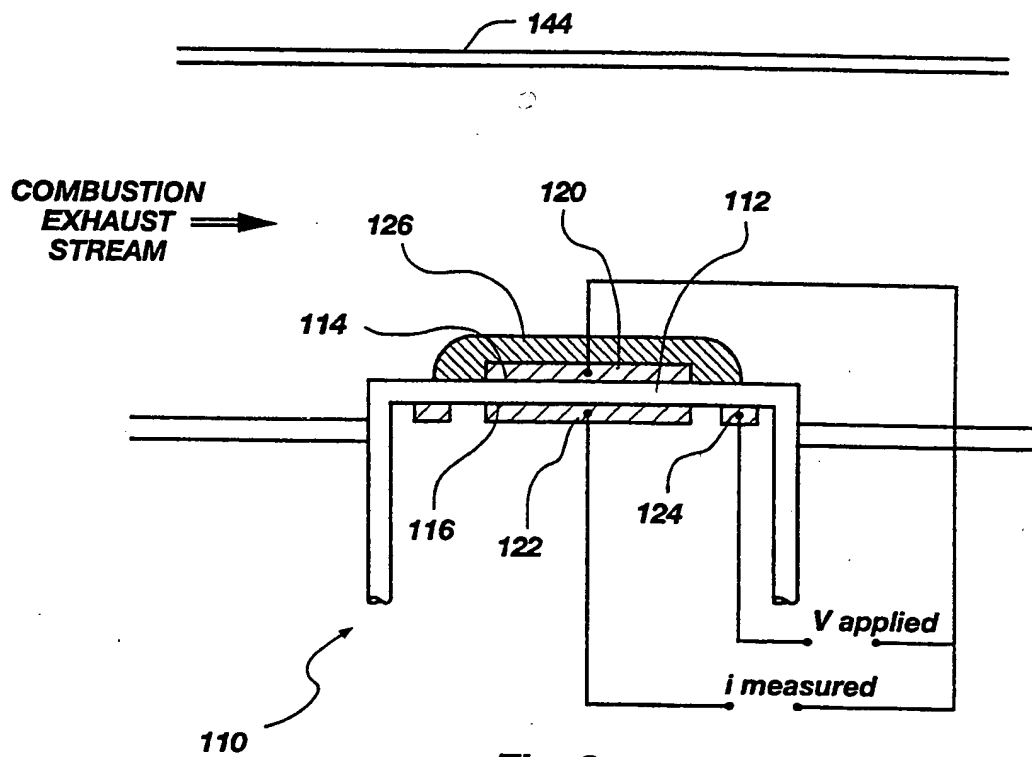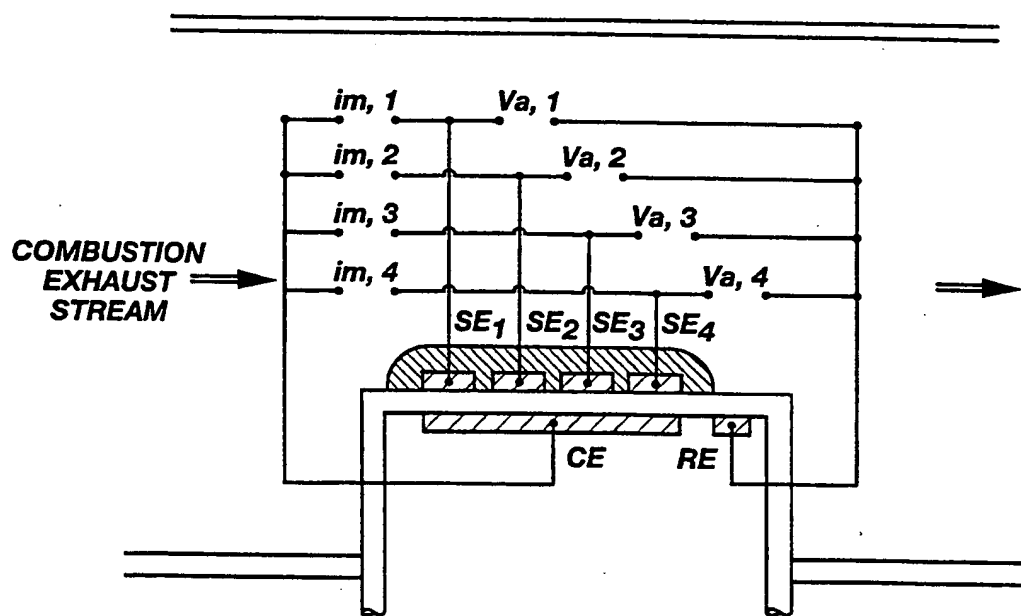
Fig. 3

3/17
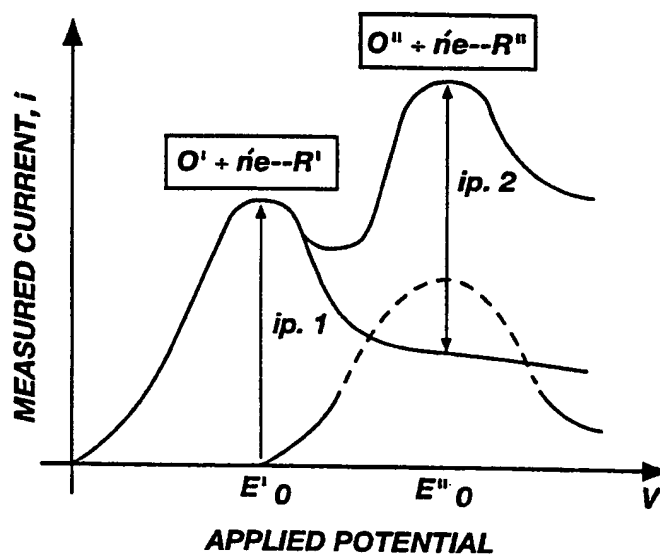
Fig. 4
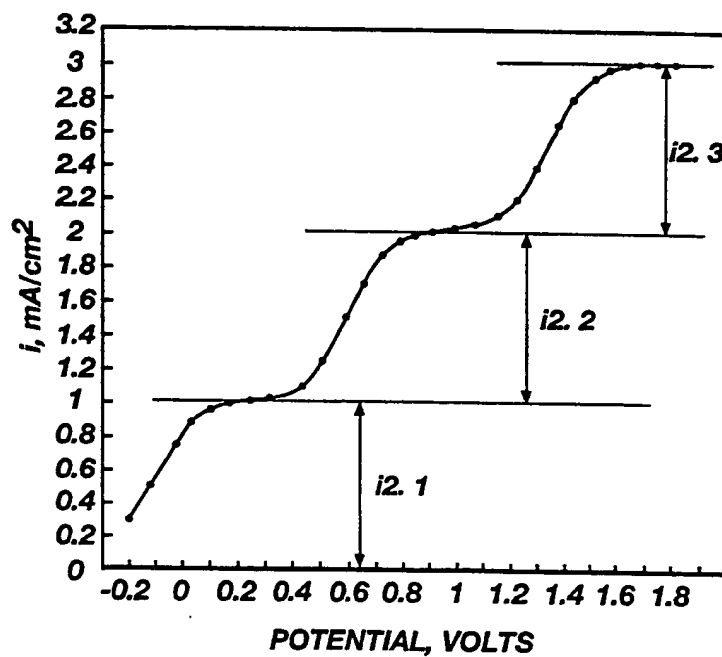
Fig. 5

SUBSTITUTE SHEET (RULE 26)
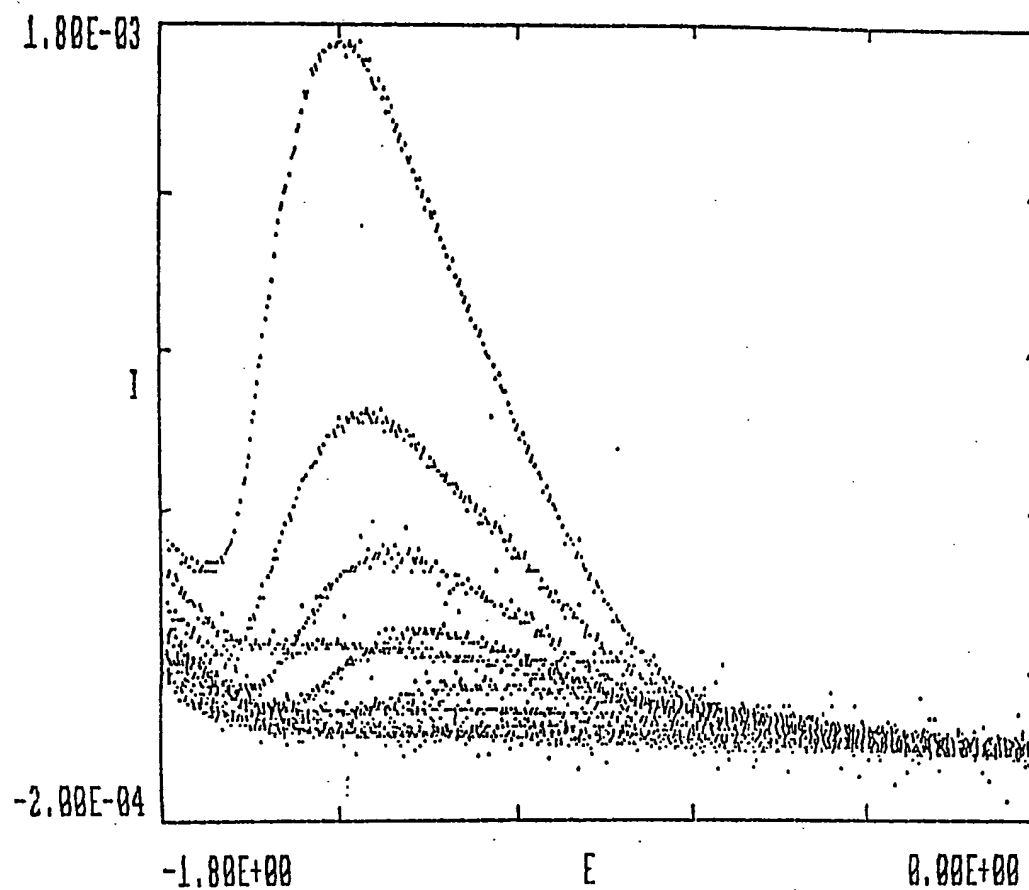
FIG. 6
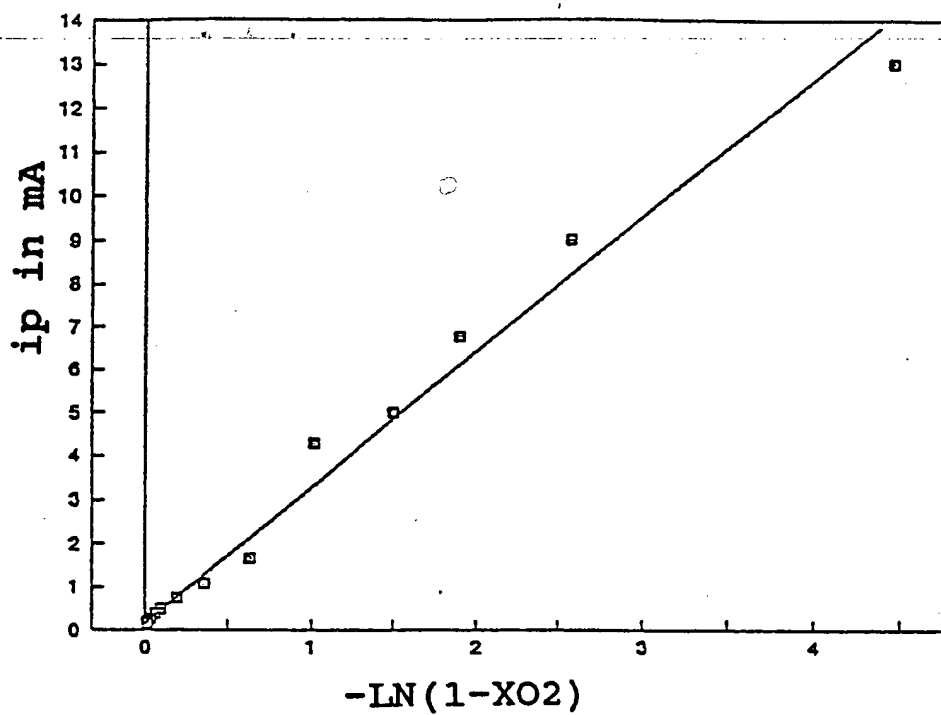
FIG. 7
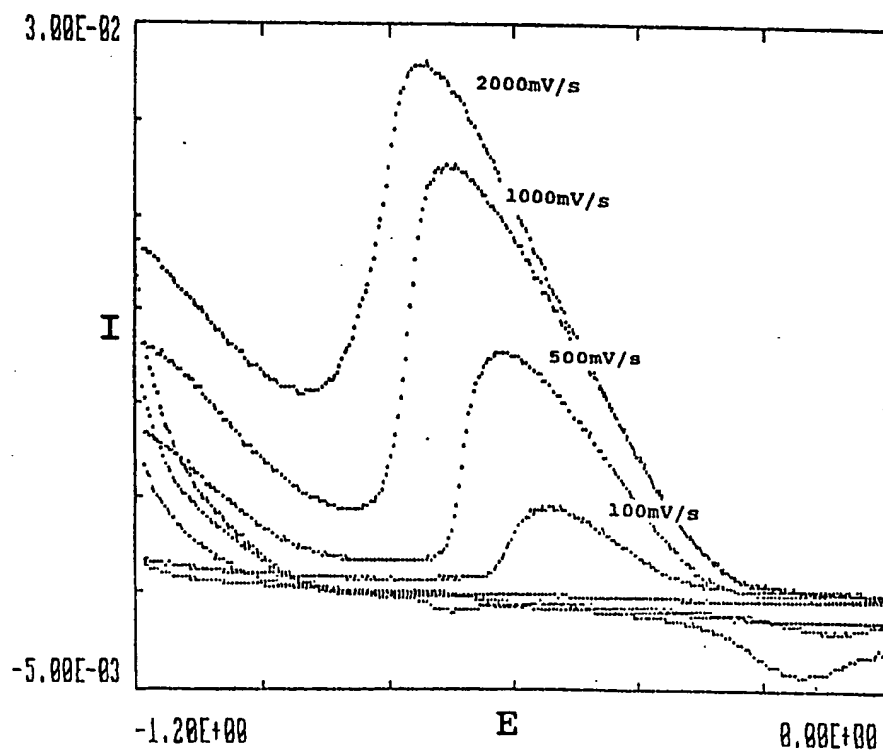
FIG. 8
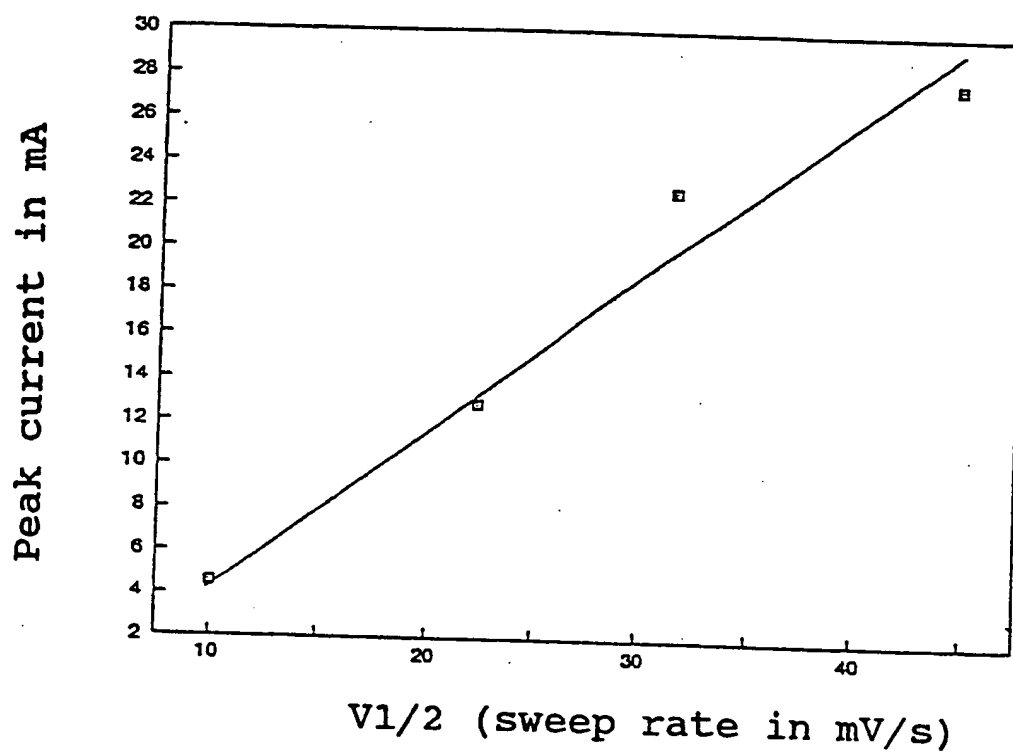
FIG. 9
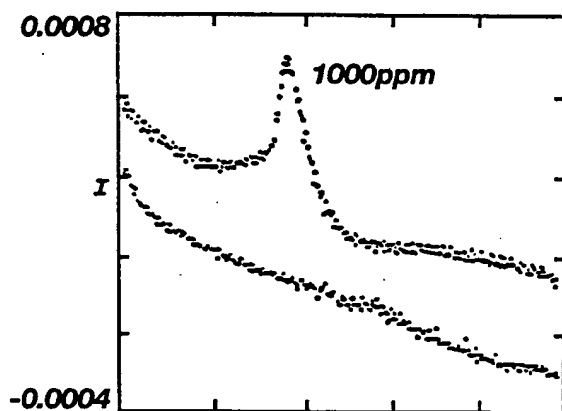
Fig. 10
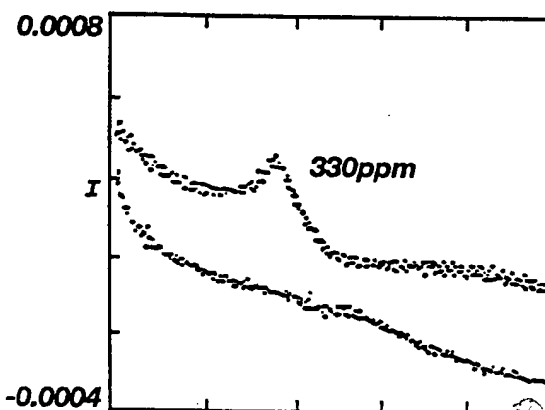
Fig. 11

Fig. 12

Fig. 13
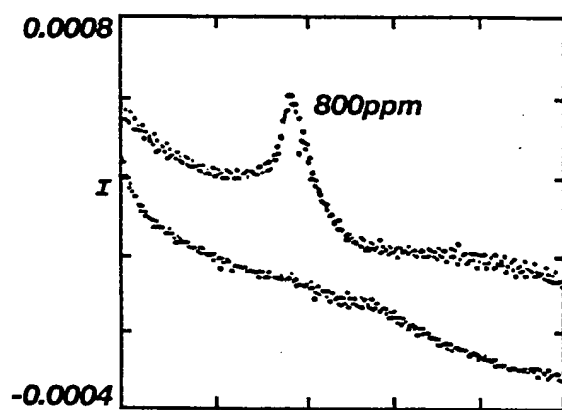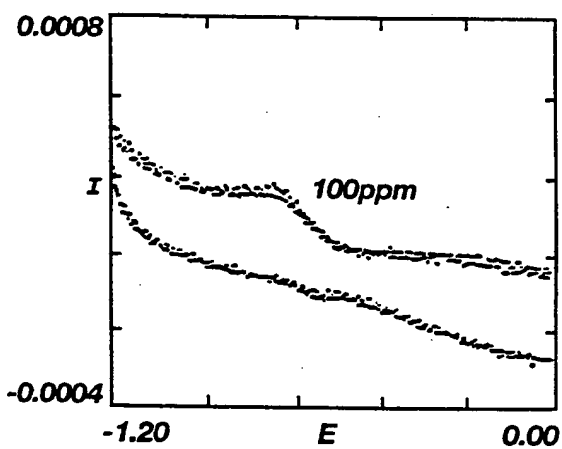
Fig. 14
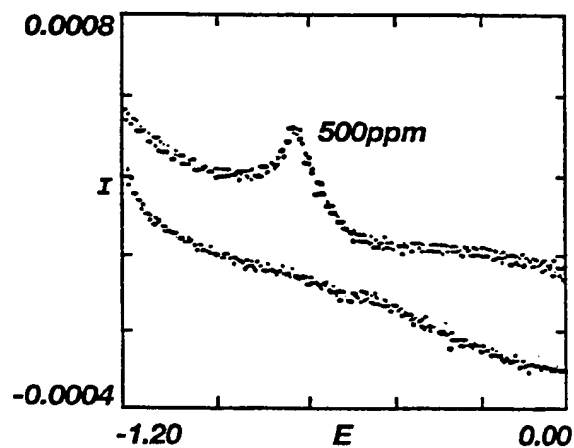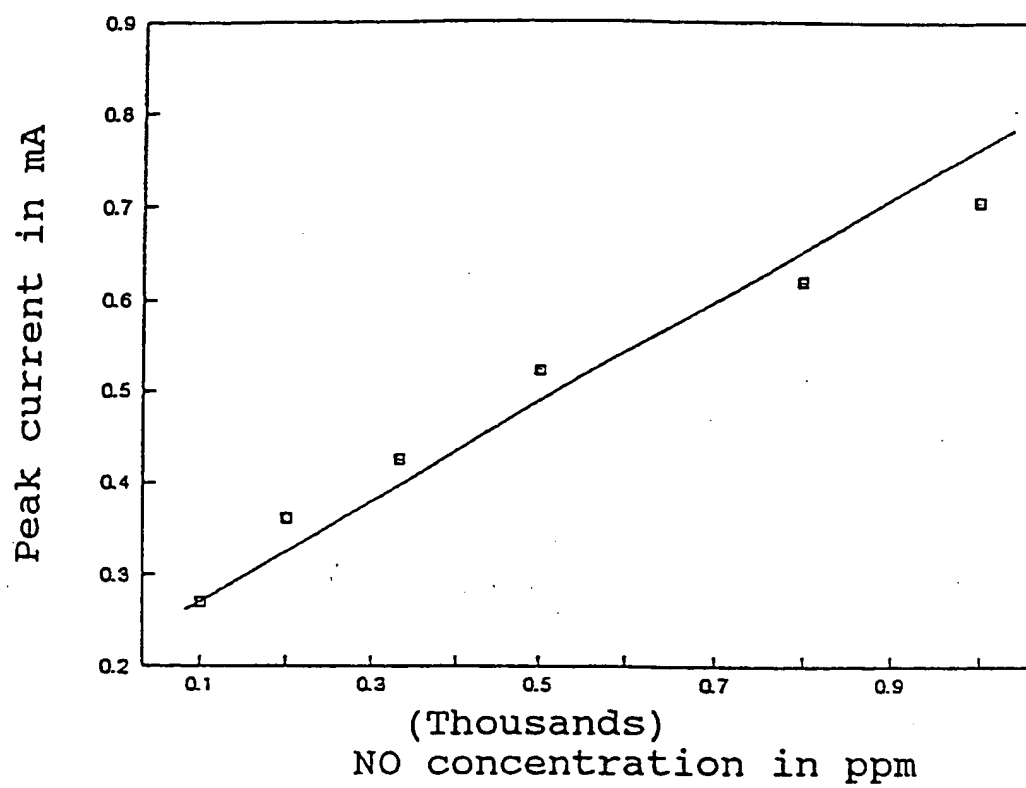
Fig. 11A
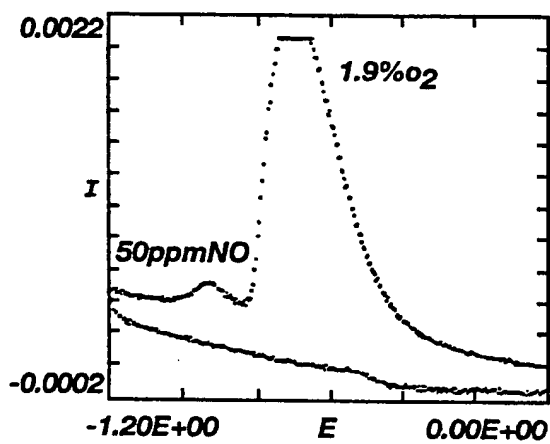
Fig. 15
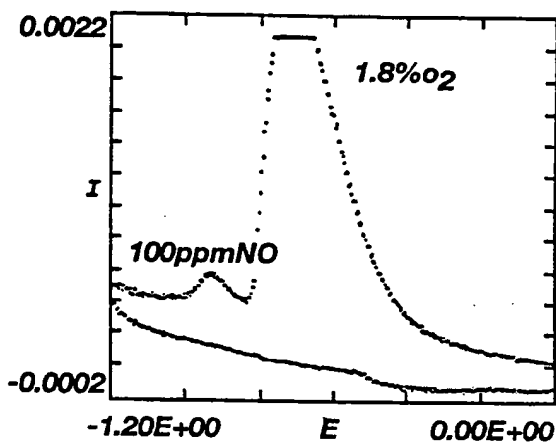
Fig. 16
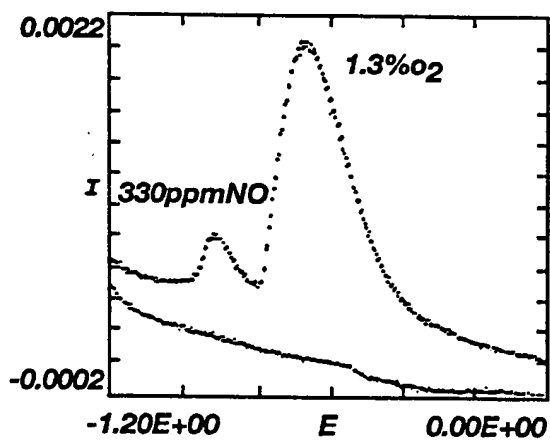
Fig. 17
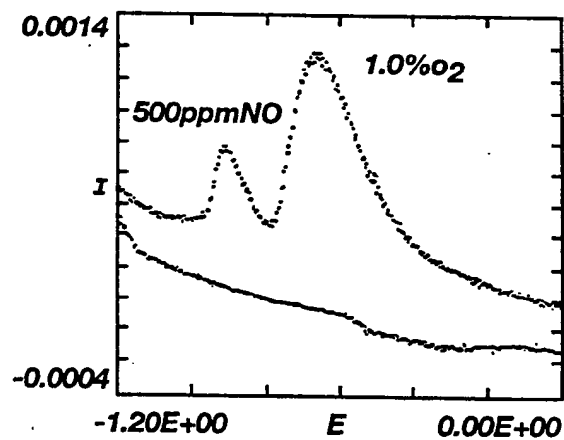
Fig. 18
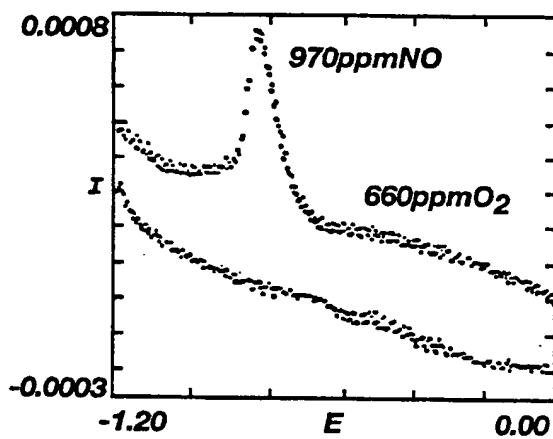
Fig. 19
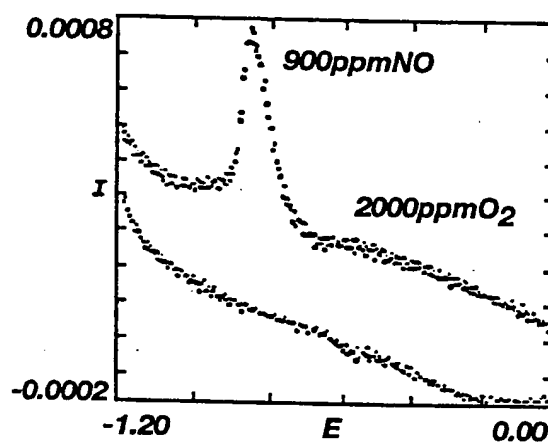
Fig. 20
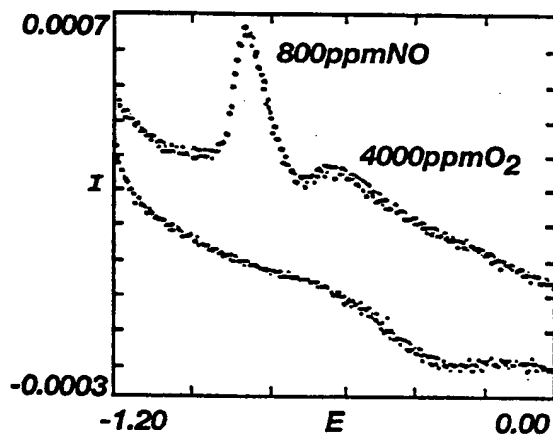
Fig. 21
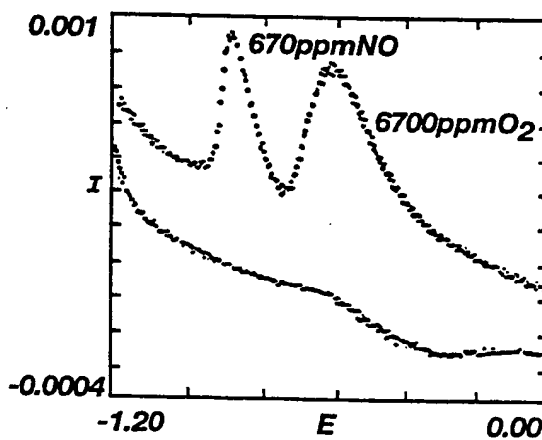
Fig. 22
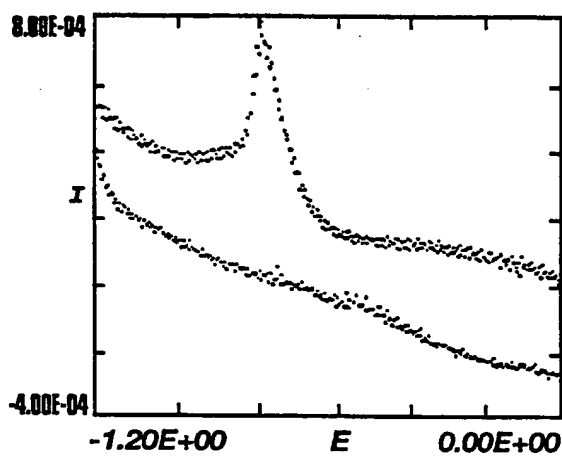
Fig. 23
500°C
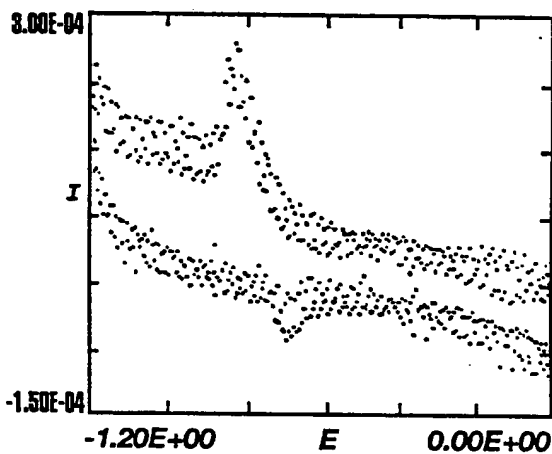
Fig. 24
450°C
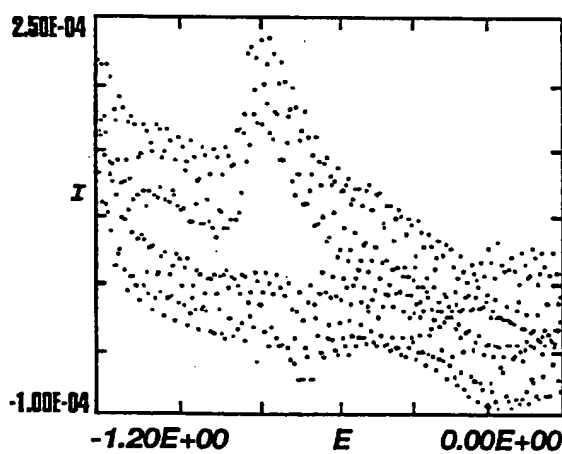
Fig. 25
400°C
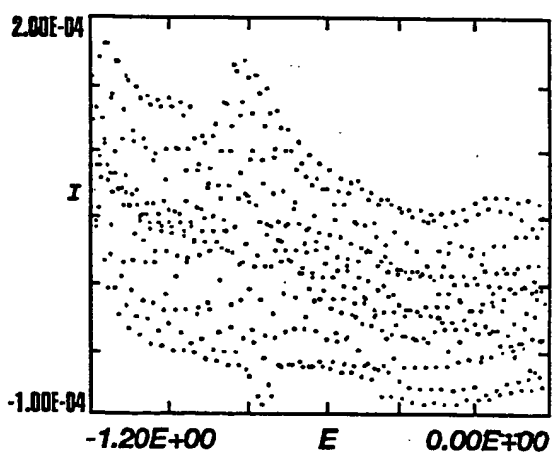
Fig. 26
350°C
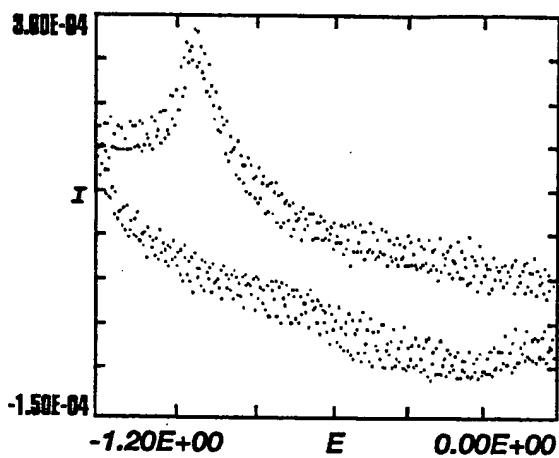
500ppm NO + N₂

Fig. 27
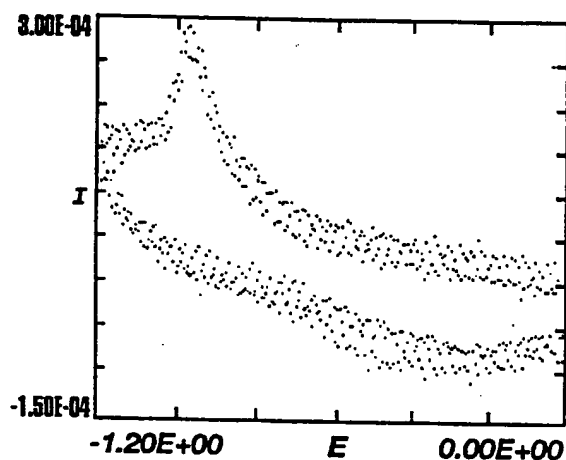
500ppm NO + 10% CO₂

Fig. 28
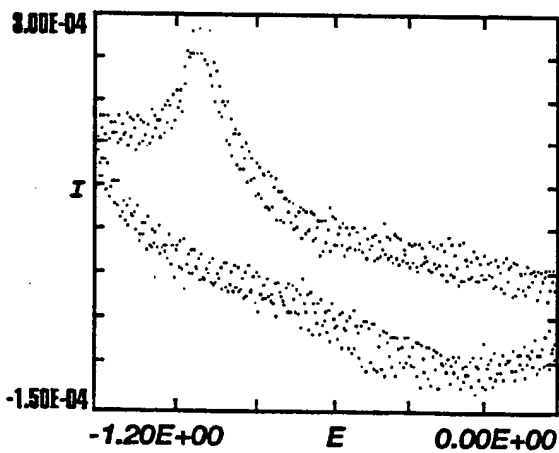
500ppm NO + 500ppm CH₄

Fig. 29
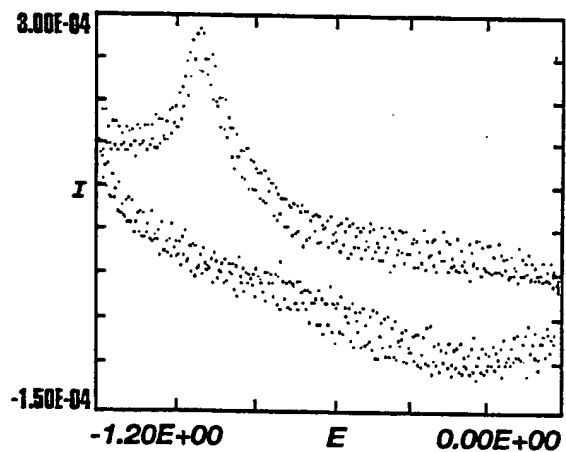
500ppm NO + 500ppm CO

Fig. 30

13/17
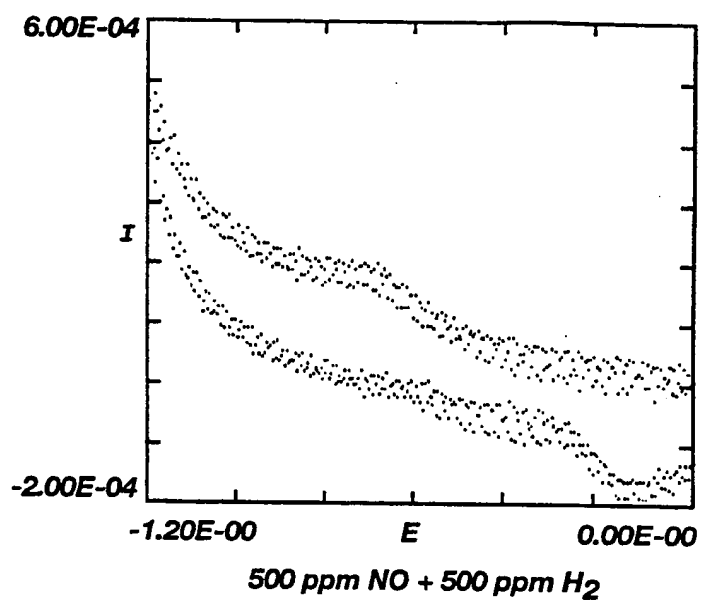
500 ppm NO + 500 ppm H$_2$

Fig. 31

500 ppm NO + 500 ppm H$_2$ + 0.7% O$_2$

Fig. 32

500ppm NO (dry)

Fig. 33

500ppm NO + 3% H_2O

Fig. 34

500ppm NO + 25% H_2O

Fig. 35

500ppm NO (dry), after sensor
tested in moisture environment
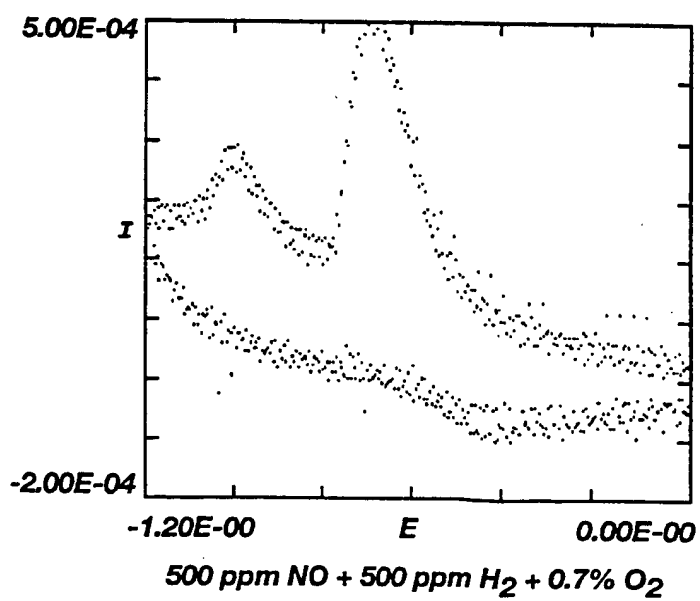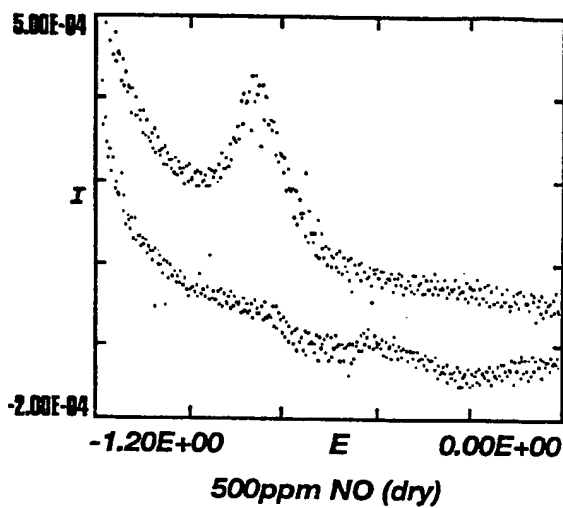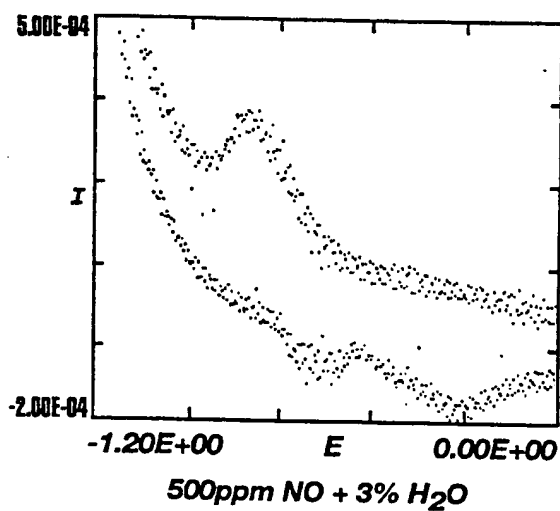
Fig. 36
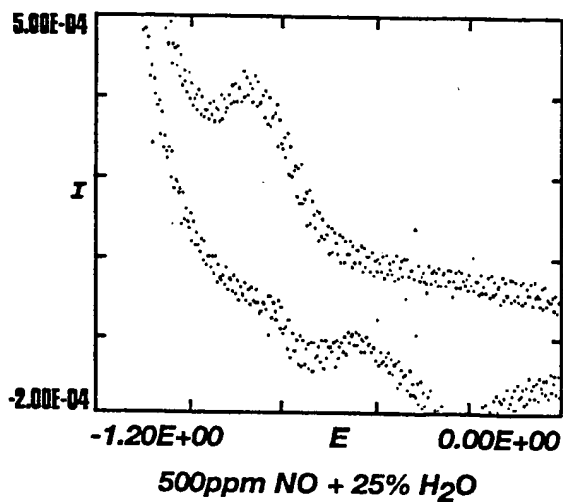
Fig. 37
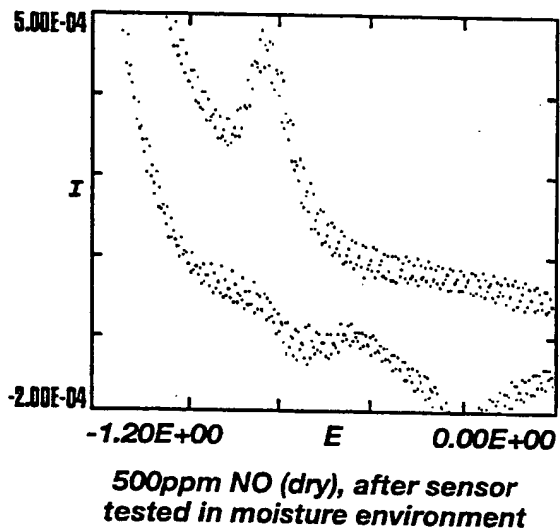
100ppm NO
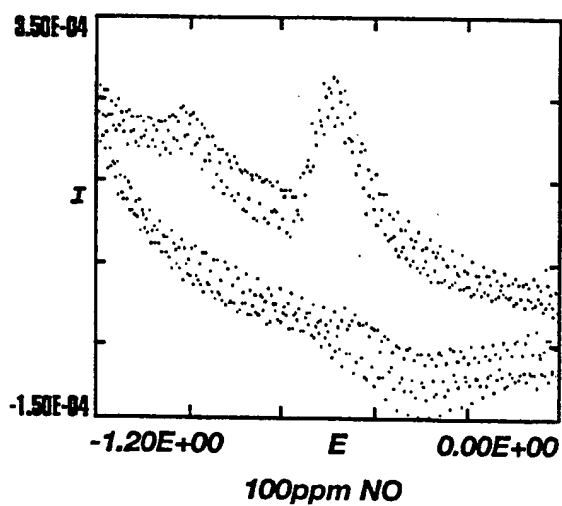
Fig. 38
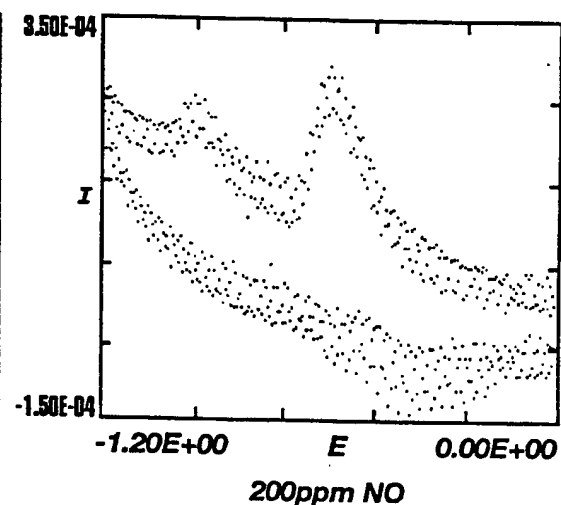
200ppm NO
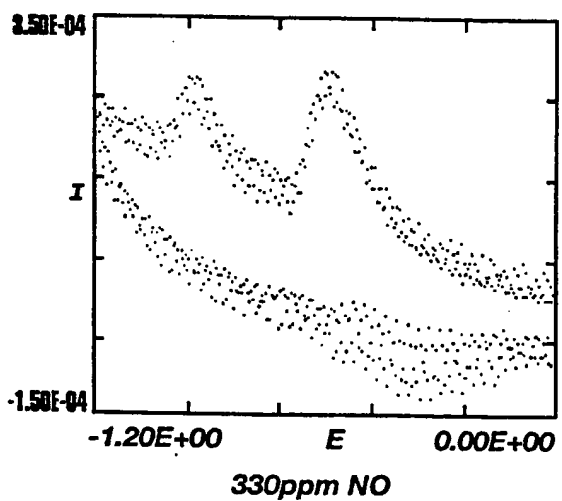
Fig. 39
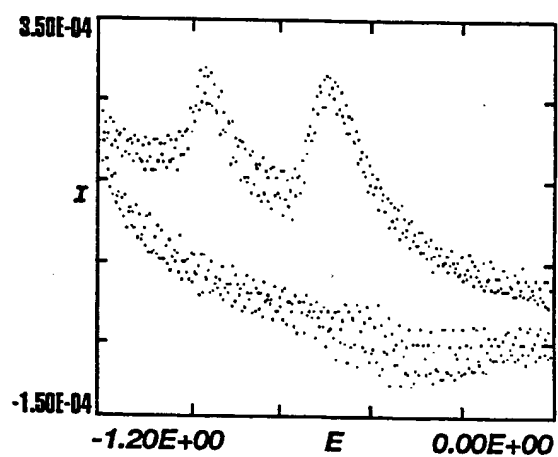
330ppm NO

Fig. 40
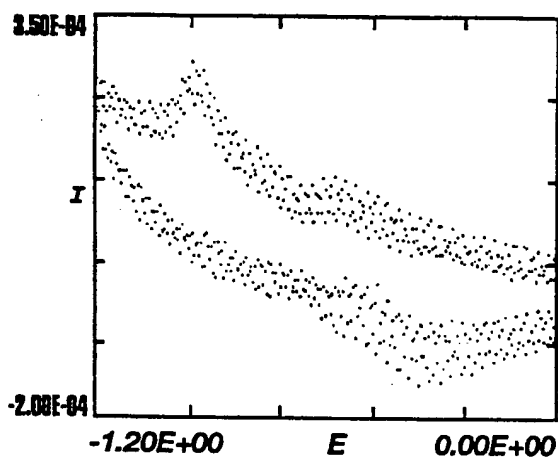
500ppm NO

0.2% O$_2$

Fig. 41
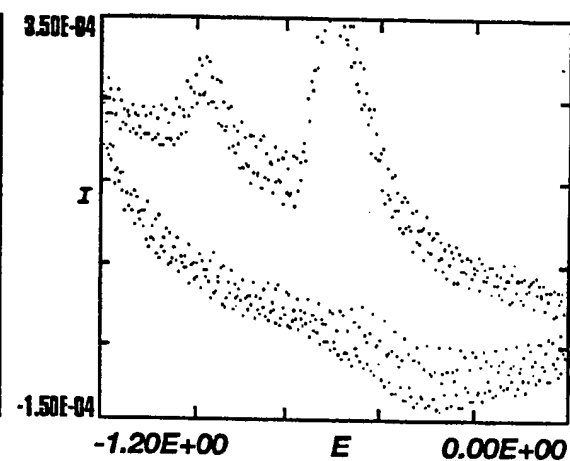
0.67% O$_2$

Fig. 42
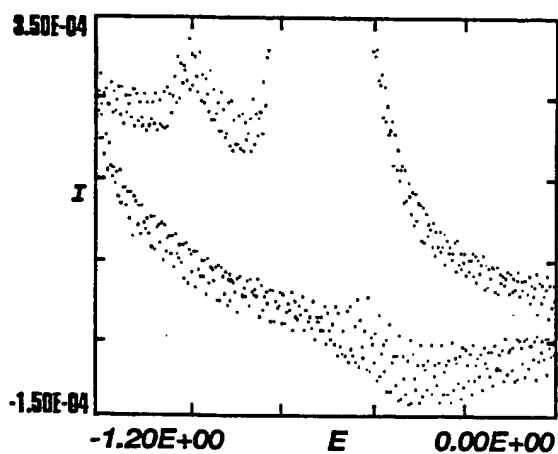
2.1% O$_2$

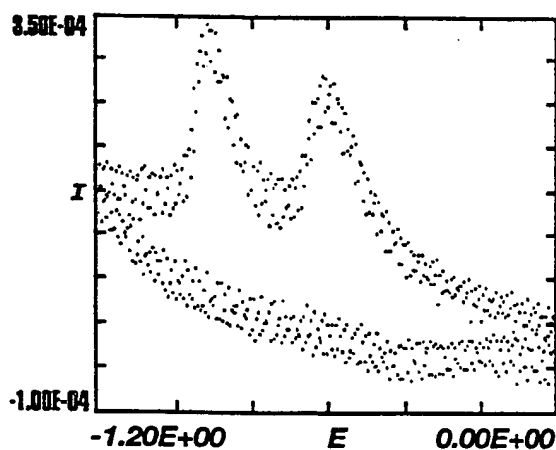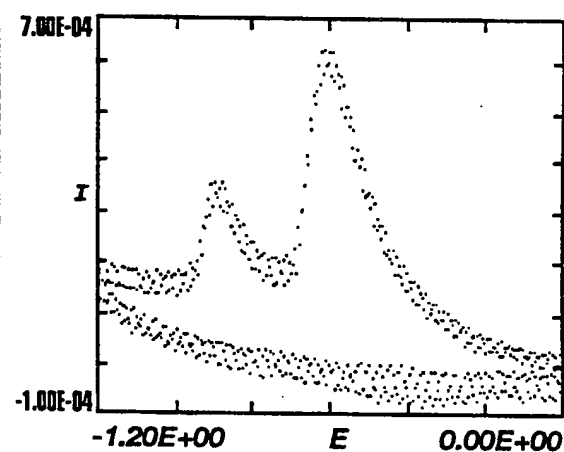**Fig. 43**
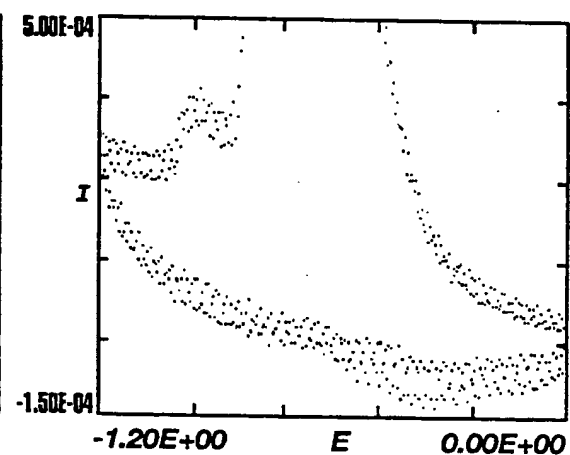
4.2% O$_2$

Fig. 44
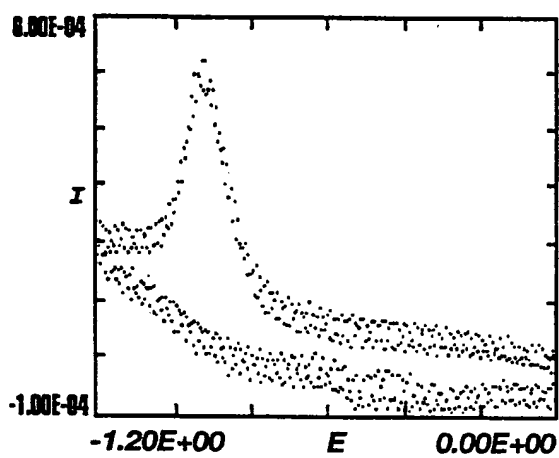
(a) 1000 ppm NO

Fig. 45
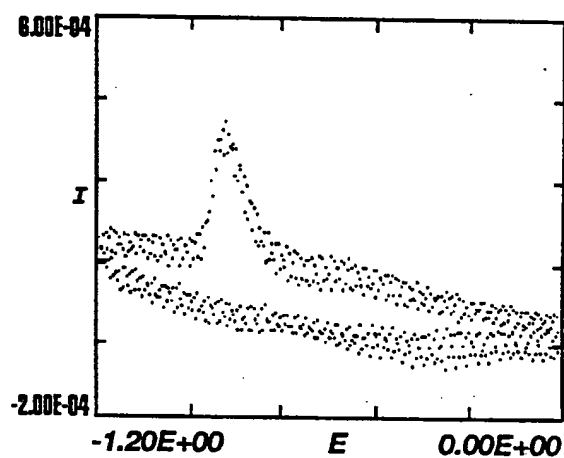
(b) 1000 ppm NO

Fig. 46

(c) 800 ppm NO + 0.4% O_2

Fig. 47

(d) 800 ppm NO + 0.4% O_2

Fig. 48

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : G01N 27/407
US CL : 204/412

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/153.18, 410, 411, 412, 421, 422, 423, 424, 425. 426. 427. 428,429

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A 3,989,614 (Tien), 02 November 1976, see figure 3 and column 3, line 61 to column 4, line 52.	1 - 5 , 7 - 11,13,14,17
A	US,A, 4,292,158 (Muller et al), 29 September 1981, see figure 1 and column 2, line 17 to column 2, line 25.	1-17
A	US,A, 4,298,573 (Fujishiro), 03 November 1981, see figure 12 and column 11, lines 6-69.	1-17
Y	US,A, 4,306,957 (Ishitani et al), 22 December 1981, see column 17, lines 4-22).	1 - 5 , 7 - 11,13,14,17
A	US,A, 4,522,690 (Venkatasetty), 11 June 1985, see column 2, lines 23-38.	1-17

[X] Further documents are listed in the continuation of Box C.   [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 MARCH 1994	APR 04 1994

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	T. TUNG
Facsimile No. (703) 305-3230	Telephone No. (703) 308-3329

Form PCT/ISA/210 (second sheet)(July 1992)*

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,570,479 (Sakurai et al), 18 February 1986, see figure 4 and column 4, lines 57-62.	1-5,7-11,13,14,17
A	US,A, 5,173,166 (Tomantschger et al), 22 December 1992, see figure 4 and column 8, lines 38-54	1-17